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De vorming van monoterpenen en pentadekanolide in de vluchtige olie van angelica archangelica L.

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SAMENVATTING

Het doel van dit onderzoek was de samenstelling van de vluchtige olie uit de wortel van *Angelica archangelica* L. nader te onderzoeken en zo mogelijk uit de verhouding van de terpenen in verschillende ontwikkelingsstadia van de plant tot een hypothese over de vorming van deze bestanddelen te komen.

Na een historische inleiding over *Angelica archangelica* L. werden de plant, de teelt en de verwerking in het kort besproken.

Hierna werd een literatuuroverzicht gegeven van de chemische samenstelling der angelica-olie, waarin tevens andere soorten en variëteiten werden betrokken.

Vervolgens werden de toe te passen chemische methodieken bestudeerd. De kwalitatieve bepalingsmethode van de monoterpenen berust op het vaststellen van relatieve retentievolumina t.o.v. limoneen op vijf stationaire fasen van verschillende polariteit. In verband met het mogelijke voorkomen in angelica-wortelolie werden van de volgende tweeëntwintig terpenen de retentievolumina bepaald; myrceen, cis-ocimeen, trans-ocimeen, cis-alloëcimeen, trans-alloëcimeen, α -terpineen, γ -terpineen, α -felandreen, β -felandreen, limoneen, terpinoleen, p-cymeen, α -pineen, β -pineen, α -thujeen, sabineen, 3-careen, kamfeen, α -fencheen, β -fencheen, santeen en tricycleen. De acyclische, monocyclische en bicyclische terpenen vertonen hierbij een onderling afwijkend gaschromatografisch gedrag. Behalve de in de literatuur genoemde terpenen α -pineen en α -felandreen konden verder in angelica-wortelolie worden aangetoond: β -felandreen, 3-careen, limoneen, myrceen, cis- en trans-ocimeen, p-cymeen, terpinoleen, β -pineen, sabineen, γ -terpineen en kamfeen en/of α -fencheen.

De kwalitatieve bepaling van deze terpenen berust op de interne standaardmethode, waarbij n-dekaan als standaard fungeert. De waarde piekhoogte \times retentietijd bleek in ons geval de beste maatstaf voor de hoeveelheid van de component. Omdat "slechts" veertien à vijftien monoterpenen in de olie voorkomen, kon het kwantitatieve onderzoek worden uitgevoerd op twee stationaire fasen, nl. carbowax-4000 en β , β' -oxydipropionitril.

De kwantitatieve bepaling van pentadekanolide werd uitgevoerd met het homologe hexadekanolide als interne standaard.

Hoewel niet tot het directe doel van dit onderzoek behorend, werden enkele zuurstofbevattende verbindingen geïdentificeerd, n.l. borneol en carvacrol.

Van de gevonden terpenen en pentadekanolide werden de absolute hoeveelheden per plant in de hoofdwortel en de bijwortels berekend. Het bleek, dat de vorming van vluchtige olie, die reeds in een zeer vroeg stadium begint, vooral plaatsvond in de eerste groeistadia, terwijl de hoeveelheid aan het einde der onderzochte periode nagenoeg konstant was geworden.

Op grond van verhoudingsgetallen tussen terpenen en terpeengroeperingen onderling kwam naar voren, dat de groepen [myrceen, cis- en trans-ocimeen], [limoneen, terpinoleen en α -pineen] en [3-careen, α - en β -felandreen] onderling bijbehorende terpenen bevatten. De eerste groep van verbindingen kan

men zich ontstaan denken uit het linalylcarboniumion door protoneliminatie. De tweede groep van terpenen kan men zich ontstaan denken uit het α -terpenylcarboniumion, eveneens door protoneliminatie. De biogenetische vormingswijzen van de, in kwantiteit belangrijkste, terpenen van de laatste groep week blijkens de resultaten van het onderzoek, af van die der beide eerste groepen. Een mogelijke vormingswijze van α -felandreen - en eventueel 3-careen - uit een "precursor" van cis-ocimeen werd overwogen. Voor de vorming van β -felandreen kon met de huidige gegevens geen bevredigende formulering worden opgesteld.

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SUMMARY

The purpose of this investigation was to further examine the composition of the essential oil from the root of *Angelica archangelica* L. and if possible to come to a hypothesis on the formation of the terpene-compounds from the proportion in the different stadia of development.

A historical introduction on *Angelica archangelica* L. is followed by a short description of the plant, its cultivation and the working up.

A review is given of the literature concerning the chemical composition of angelica-oil, together with other species and varieties.

In chapter IV analytical methods are studied. The monoterpenes are determined qualitatively by their relative retentionvolumes with respect to limonene as found by gaschromatography on five stationary phases of different polarity. In connection with the possible occurrence in angelica-rootoil retentionvolumes of the following twenty two terpenes were determined: myrcene, cis- and trans-ocimene, cis- and trans-alloöcimene, α - and γ -terpinene, α - and β -phellandrene, limonene, terpinolene, p-cymene, α - and β -pinene, α -thuyene, sabinene, 3-carene, camphene, α - and β -fenchene, santene and tricyclene. The groups of the acyclic, monocyclic and bicyclic terpenes can be distinguished gaschromatographically. Beside the terpenes mentioned in the literature i.e. α -pinene and α -phellandrene, we found the following components in angelica-rootoil: β -phellandrene, 3-carene, limonene, myrcene, cis- and trans-ocimene, p-cymene, terpinolene, β -pinene, sabinene, γ -terpinene, together with camphene and/or α -fenchene.

Quantitative determination of these terpenes is based on the internal standard method, with n-decane as a standard. We found that the product of peakheight and retention-time is the best quantitative measure for each component. Because "only" fourteen to fifteen monoterpenes are present in the oil, we were able to carry out the quantitative investigation on two stationary phases viz. carbowax-4000 and β , β' -oxydipropionitrile.

Quantitative determination of pentadecanolide was carried out with the homologous hexadecanolide as an internal standard.

Though not directly adhering to this investigation, some oxygen-containing compounds were identified viz. borneol and carvacrol.

For all constituents i.e. terpenes and pentadecanolide the absolute quantities per plant in the main root and the side roots were calculated. It was shown that the amount of volatile oil, the formation of which starts already at a very early stage, increased strongly particularly in the initial growth stages, while at the end of the period under investigation, these amounts reached a constant level.

On the strength of ratios between terpenes and terpene groups it could be shown that the groups [myrcene, cis- and trans-ocimene], [limonene, terpinolene and α -pinene] and [3-carene, α - and β -phellandrene] contain "genetically" related terpenes. The first group of compounds can formally be thought to arise from linalylcarbonium-ion by proton-elimination. The second group of terpenes can be formed through the α -terpenylcarbonium-ion,

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also by proton-elimination. According to our experimental results the biosynthesis of the quantitatively most important terpenes of the last group differed from that of the first two groups. A possible biosynthesis of α -phellandrene — and perhaps 3-carene — from a precursor of cis-ocimene was taken into consideration. For the formation of β -phellandrene no satisfactory route could as yet be suggested.

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